INFRA-RED ABSORPTION SPECTRA OF SOLUTIONS OF ETHYLENE DICHLORIDE IN CERTAIN SOLVENTS*

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ABSTRACT. The infra-red absorption spectra of pure ethylene dichloride and of its solutions in carbon tetrachloride, methyl cyclohexane and heptane of different concentrations recorded with a Perkin-Elmer Model 21 spectrophotometer have been compared with each other. The integrated intensities of the absorption peaks 1297 cm^{-1} and 1236 cm^{-1} have been measured in each case and it is observed that in the case of 20% solutions in heptane and methyl cyclohexane the ratio A_{1297}/A_{1236} is less than that for the pure liquid and that the ratio diminishes by about 50% when the strength of the solution is diminished to 3%. In the case of solutions in CCl_4 the changes in the ratio mentioned above are much smaller.

The spectra due to 5% solution of $C_2H_4Cl_2$ in heptane were recorded with the solution at 27°C and 70°C and it was observed that the ratio is slightly smaller at higher temperature than at the room temperature.

It is pointed out that such changes in the ratio A_{1297}/A_{1236} are in complete disagreement with those expected from the energy-difference of the two types of molecules in the solution calculated by previous workers. It is concluded that the results can be explained on the assumption that formation of virtual H–Cl linkages in the liquids is responsible for the origin of the gauche molecules.

INTRODUCTION

The existence of rotational isomers in the liquid state of some substituted ethane compounds was first demonstrated by Mizushima and Morino (1938). From the values of dielectric constant of gaseous ethylene dichloride Watanabe *et al.* (1942) found the difference of energy between the trans and gauche configurations of the molecule to be 1.22 KCal/mole, and taking into account the respective partition functions and also the two alternative configurations of the gauche molecule, they calculated the ratio of the number of gauche and trans molecules and found it to be 0.34 : 1 in the vapour state at the boiling point of the liquid. By comparing the intensities of the Raman lines 666 cm^{-1} and 768 cm^{-1} both in the case of vapour state and also for the liquid state they concluded that the value of the ratio of gauche and trans molecules in the liquid state is 1.3 : 1. Watanabe *et al.* (1943) tried to explain this change in the ratio of population of the two types of molecules with change of state by assuming

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that in the liquid state the gauche molecule acquires an excess of electrostatic energy which is equal to $-\left(\frac{\epsilon-1}{2\epsilon+1}\right)\frac{\mu^2}{a^3}$, where ϵ is the dielectric constant of the liquid, μ the permanent electric moment of the gauche molecule and a is its radius assuming the molecule to be a sphere. They showed that the influence of this electrostatic energy would diminish the energy-difference of the two types of molecules to a very small value in the liquid state. Actually, from the temperature-dependence of the ratio of intensities of the lines mentioned above they concluded that the electrostatic energy of the gauche molecules in the liquid state explains the observed change in energy-difference.

From the results of measurements of the infra-red absorption bands 1235 cm^{-1} and 1291 cm^{-1} of ethylene dichloride in the vapour state at different temperatures Bernstein (1949) concluded that the ratio (N_g/N_t) of the gauche (C_2) and trans (C_{2h}) molecules increases at higher temperatures indicating an energy-difference of about 1140 cal/mole between the two configurations. The value of N_g/N_t at 424.4°K was found by him to be 0.574, while from the ratio of the intensities of the Raman lines 666 cm^{-1} and 768 cm^{-1} in the vapour state at 443°K Watanabe *et al* (1943) found the value of N_g/N_t to be 0.47. The present author (1953) also measured the ratio of the intensities of the two Raman lines due to ethylene dichloride at 135°C and found it to be 1 · 4.5. When these results were compared with those published by Watanabe *et al* (1943), the change in the ratio of intensity of the two lines mentioned above with change of temperature of the vapour indicated very small energy-difference of the two types of molecules. Thus these results are at variance with each other.

Rank, Kagarise and Axford (1949) found the value of energy-difference of the two types of molecules in the liquid state to be almost zero. This would lead to a value of N_g/N_t equal to 1.90 according to Watanabe *et al* (1942). Actually, however, with the value of the energy-difference deduced from the dielectric measurements and from the ratio of intensities of the Raman lines 666 cm^{-1} and 768 cm^{-1} of ethylene dichloride in the vapour and liquid states, they got the value 1.3 · 1 for N_g/N_t in the liquid state. So the value of N_g/N_t found out by Watanabe *et al* is not in agreement with the value of energy-difference in the liquid state reported by Rank *et al*.

It was suggested earlier by Bishui (1948) that the gauche type of molecule of ethylene dichloride in the liquid state might be produced by association of the neighbouring molecules. Kuratani (1952), however, studied the infra-red absorption bands of ethylene dichloride in solution in a few solvents and measured the intensity-ratio of the absorption bands 1284 cm^{-1} and 1230 cm^{-1} and found that the ratio did not change with the change of concentration of the solution. From these results he concluded that the band 1284 cm^{-1} was not produced by associated molecules as suggested by Bishui (1948). Later, Banerjee (1954)

measured the intensities of the Raman lines 654 cm^{-1} and 755 cm^{-1} of ethylene dichloride dissolved in more suitable solvents such as heptane and cyclohexane with different concentrations ranging from 35% to 65% and found that the ratio of intensities of the two lines diminishes with the diminution of concentration of the solutions. From these results he concluded that when suitable solvents are used some of the associated groups which produce the gauche type of molecule break up into single molecules and the number of gauche molecules is thus reduced at higher dilutions.

Kuratani (1952) measured the ratio of intensities of the infra-red absorption bands 1284 cm^{-1} and 1230 cm^{-1} of the solutions of ethylene dichloride in benzene, CCl_4, CS_2 and acetonitrile of different concentrations. If, however, the ratio of the intensities of the same infra-red absorption bands were measured for the solutions in some other suitable solvents the results might show more conclusively whether the ratio of the intensity of the bands due to the two types of molecules changes with concentration or not. For this reason, the investigation of the ratio of intensities of the infra-red absorption bands of solutions of ethylene dichloride of different concentrations in heptane, methyl cyclohexane and CCl_4 was undertaken and the results have been discussed in the present paper. The solvents heptane and methyl cyclohexane were chosen to find out whether at concentrations lower than those used by Banerjee (1954) any remarkable changes occur in the ratio N_g/N_t.

EXPERIMENTAL

Chemically pure ethylene dichloride obtained from E. Merck was dehydrated and fractionated and the fraction boiling at 83.7°C was collected and redistilled under reduced pressure. The liquids heptane, methyl cyclohexane and carbon tetrachloride were also of chemically pure quality and were distilled several times in vacuum before being used as solvents.

The strengths of the solutions in heptane and methyl cyclohexane were 3%, 10% and 20% and in CCl_4 3% and 15%.

The infra-red spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer with a sodium chloride prism. The resolution dial was placed at about 916. The absorption bands due to solvents were compensated by using suitable compensation cells in the reference beam. The thickness of the cell was 0.1 mm in the case of dilute solutions and 0.025 mm in the case of concentrated solutions. The spectra due to pure liquids were recorded by using very thin films formed between two plane parallel sodium chloride plates.

In order to find out whether the ratio of the intensities of the bands 1236 cm^{-1} and 1297 cm^{-1} of ethylene dichloride solutions changes with change of temperature of the solution the spectrum due to 5% solution in heptane at 70°C was recorded and compared with that recorded for the solution at 27°C.

RESULTS AND DISCUSSION

The values of A_{1297}/A_{1236} of pure ethylene dichloride and its solutions in carbon tetrachloride and methyl cyclohexane at 27°C and in heptane at 27°C and 70°C are given in Table 1. The absorption curves due to the pure liquid, 15% and 3% solutions in CCl_4, and 20%, 10% and 3% solutions in methyl cyclohexane and heptane are reproduced in figures 1, 2, 3 and 4 respectively. Figure 5 shows the absorption curves due to 5% solution of ethylene dichloride in heptane at 27°C and 70°C.

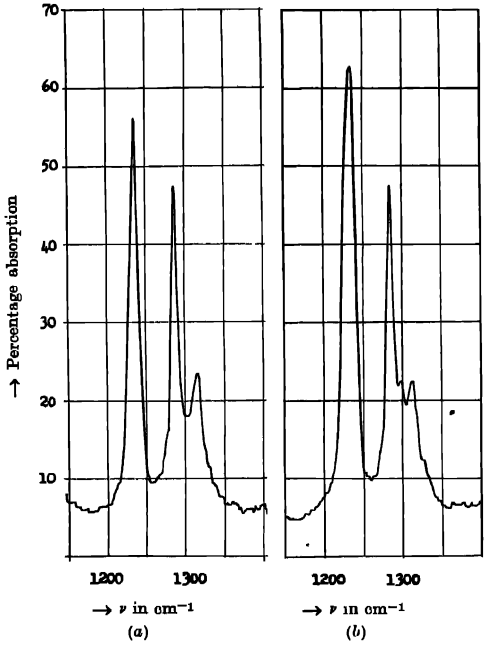

Fig. 1. Infra-red absorption curves of pure ethylene dichloride.
(*a*) Thin film of the liquid. (*b*) Thin film under slight pressure.

In the case of pure liquid it was found that the band 1297 cm^{-1} split up into three components in some cases and into two components in other cases, the three components appearing only when the cell was extremely thin and the liquid film was under slight pressure and two components in the case of thicker films or solutions. When the ratio of the integrated intensities of all the components of the band 1297 cm^{-1} to that of the band at 1236 cm^{-1} was calculated, it was found to be identical in both the cases. Apparently, however, the com-

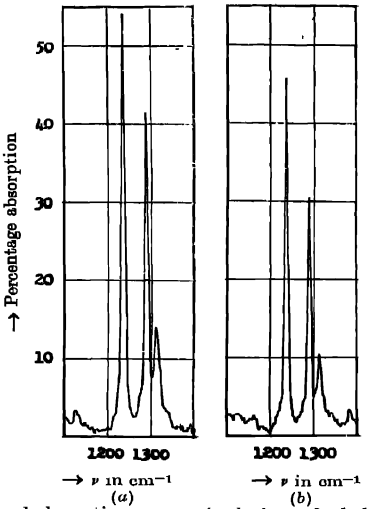

Fig. 2. Infra-red absorption curves of solutions of ethylene dichloride in carbon tetrachloride.
(*a*) 15% solution in 0.025 mm cell. (*b*) 3% solution in 0.1 mm cell.

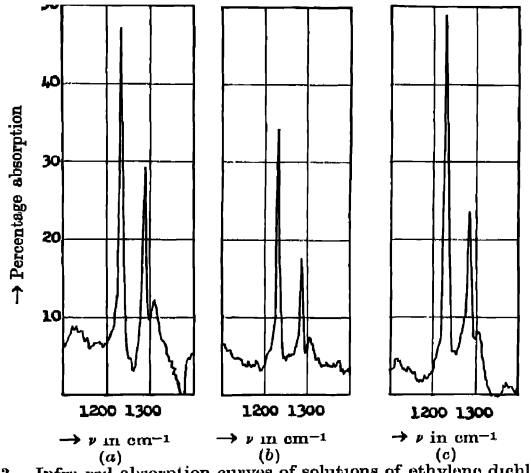

Fig. 3. Infra-red absorption curves of solutions of ethylene dichloride in methyl cyclohexane.
(*a*) 20% solution in 0 025 mm cell.
(*b*) 10% „ „ „ „
(*c*) 3% „ „ 0.1 mm „

ponent at 1286 cm^{-1} was found to be relatively stronger when the band 1297 cm^{-1} was split up into two components. The bands observed in both the cases are reproduced in figures 1(a) and 1(b). In calculating the relative intensities of the two bands the integrated intensity of both the components of the band 1297 cm^{-1} was taken into consideration.

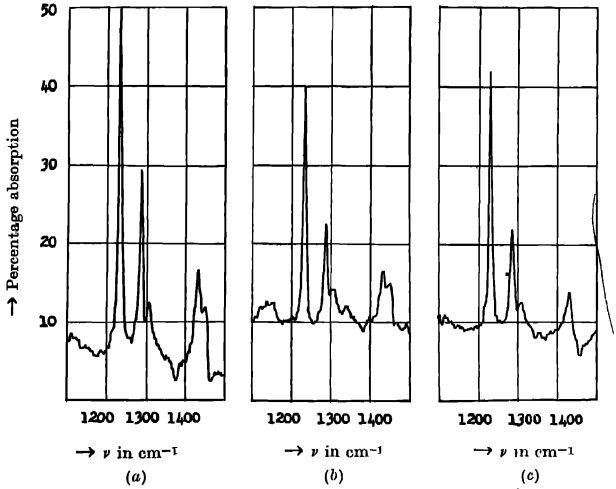

Fig. 4. Infra-red absorption curves of solutions of ethylene dichloride in heptane.

(a) 20% solution in 0 025 mm cell.
(b) 10% „ „ 9 025 mm „
(c) 3% „ „ 0.1 mm „

It can be seen from Table I that the ratio A_{1297}/A_{1236} changes very slightly when ethylene dichloride is dissolved in CCl_4 to make a 15% solution and that the ratio diminishes again very slightly when the solution is diluted to 3%. The ratio, however, changes more markedly when the liquid is dissolved either in heptane or in methyl cyclohexane even to make a 20% solution and when the solutions are diluted the ratio diminishes still further. For example, the ratio changes from 0.833 to 0.526 when pure liquid is dissolved in heptane to make a 20% solution, and the ratio is reduced to 0.357 when the strength of the solution is changed to 3%. In the cases of solutions in methyl cyclohexane also similar results are observed.

In order to understand the significance of these results it would be interesting to compare them with those expected from the values of energy-difference calculated by Wada (1954) taking into consideration the influence of different

TABLE I

Ratio of integrated absorption at the bands 1297 cm^{-1} and 1236 cm^{-1}

Solvent	Strength of solution	Temperature	A_{1297}/A_{1236}
Pure $C_2H_1Cl_2$	100%	27°C	0.833
CCl_4	3%	,,	0.645
	15%	,,	0.733
Heptane	3%	,,	0.357
	10%	,,	0.400
	20%	,,	0.526
	5%	,,	0.36
	5%	70°C	0.32
Methyl cyclohexane	3%	27°C	0 384
	10%	,,	0.476
	20%	,,	0 58

solvents on the energy-difference. He has shown that if 1270 cal/mole be taken as the energy-difference between the two types of molecules in gaseous state the value should be reduced to zero in the pure liquid. Actually also, from the measurement of temperature-dependence of the relative intensities of the Raman lines 654 cm^{-1} and 755 cm^{-1} of ethylene dichloride it has been concluded by Rank *et al* (1949) that the energy-difference in the liquid state is zero. There is, however, some difficulty about such a conclusion because the ratio N_g/N_t would be 1.9 · 1 when $\Delta E = 0$, but actually it is 1.3 : 1 as reported by Watanabe *et al* (1942). So, there is some discrepancy between the values of N_g/N_t calculated by Watanabe *et al* and that expected in the case of absence of any energy-difference (ΔE) between the two types of molecules.

In the case of solutions, the general nature of the change in ΔE due to the influence of solvent molecules calculated by Wada (1954) was shown to be in agreement with that observed experimentally by different workers. In the case of solution in CCl_4, however, the value of ΔE expected from his theory was about 790 cal/mole, but Kuratani (1952) observed the value to be 510 cal/mole. Again, the latter worker also reported that the ratio A_{1297}/A_{1236} did not change with the change of concentration of the solution, but in the present investigation it has been found that the ratio changes from 0.733 to 0.645 when the strength of the solution is changed from 15% to 3%. When there are large number of hydrogen atoms in the molecule of the solvent, such as heptane and methyl cyclohexane, the ratio mentioned above changes more rapidly with the

increase in dilution. It can be seen from Table I that the value of the ratio A_{1297}/A_{1236} for the 3% solution in heptane is even smaller than that observed in the case of ethylene dichloride vapour (Bernstein, 1949). These facts indicate that the ratio of population of the two types of molecules is not determined solely by the energy-difference, but there is some other cause which is responsible for the origin of the gauche molecules.

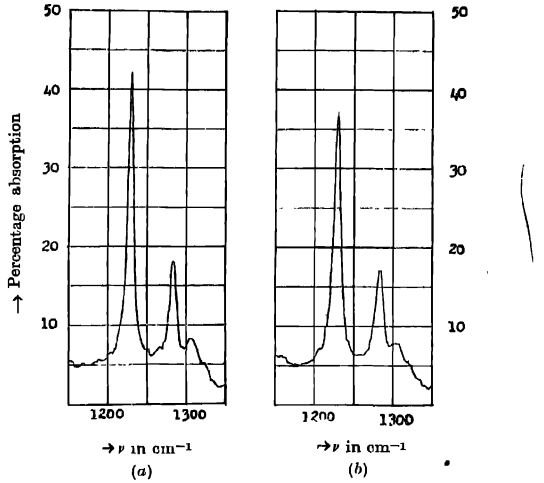

Fig. 5. Infra-red absorption spectra of 5% solution of ethylene dichloride in heptane at (*a*) 27°C and (*b*) 70°C.

In order to test the correctness of such a conclusion the temperature-dependence of the value of the ratio A_{1297}/A_{1236} in the case of 5% solution of ethylene dichloride in heptane was determined at two different temperatures of the liquid and the absorption curves reproduced in figure 5 show that the band 1236 cm^{-1} becomes a little broader at 70°C than that at 27°C. If the integrated intensities are taken into consideration the ratio mentioned above has the value 0.36 at 27°C but it diminishes to 0.32 when the temperature of the solution is raised to about 70°C. On the other hand, if the value of $\Delta E'$ were 900 cal/mole as calculated by Wada (1954), the value of A_{1297}/A_{1236} would increase and become 0.378 with the rise of temperature of the solution from 27°C to 70°C. Thus it is quite evident that the energy-difference alone does not determine the relative population of the two types of molecules in the solution.

All the results mentioned above can be explained quite satisfactorily on the hypothesis that some virtual linkage between the Cl atoms of $C_2H_4Cl_2$ molecules of the H atoms of the solvent molecules is responsible for the origin of most

of the gauche molecules present in the solution. In pure liquid also there is possibility of formation of groups of such associated molecules and this may explain the discrepancy between the observed and calculated values of the relative populations of the two types of molecules in the liquid mentioned earlier. When CCl_4 is used as a solvent there is very little tendency of the Cl atoms of the solvent molecules to break up the Cl–H linkage formed in the associated groups of $C_2H_4Cl_2$ molecules. This explains why the value of A_{1287}/A_{1236} does not change very much when ethylene dichloride is dissolved in carbon tetrachloride and also explains the large discrepancy between the value of ΔE calculated by Wada (1954) on his theory and that observed by Kuratani (1952) for this particular solution. In the case of solutions in heptane and methyl cyclohexane on the other hand, the influence of H atoms on the Cl atoms of the $C_2H_4Cl_2$ molecules is so great that the value of the ratio N_g/N_t is even less than that for the vapour. This fact furnishes an additional evidence for the fact that association between neighbouring molecules is responsible for the preponderance of the gauche molecules in the pure liquid. The results of some recent investigations in the Raman spectra of ethylene dichloride, ethylene dibromide and ethyle chlorhydrin carried out in this laboratory have furnished further evidence in support of the conclusion mentioned above These results will be discussed in a separate paper.

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